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HEAT LIBERATED IN THE LOW-TEMPERATURE OXIDATION OF ANTHRACITE

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G. S. SCOTT

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

HEAT LIBERATED IN THE LOW-TEMPERATURE OXIDATION OF ANTHRACITE[1]

By G. S. Scott[2]

INTRODUCTION

The investigation of the causes, behavior, and control of anthracite mine fires, which the Bureau of Mines has been carrying on, has yielded several publications directly applicable to mine-fire problems.[3], [4], [5], [6], [7], [8]

As a further step in elucidating the causes of heating in certain anthracites subjected to oxidation, reliable information was needed relative to the actual amount of heat that is liberated when a unit volume of oxygen combines with anthracite at varying temperatures.

At combustion temperatures, in which the products are carbon dioxide, water vapor, occasional small quantities of carbon monoxide, and ash, the net heat liberated may be determined by subtracting the heat of vaporization of the water formed from the calorific power of the fuel; and if the ash contains carbon, the percentage of ash, multiplied by its calculated calorific power, is also subtracted.

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[1] The Bureau of Mines will welcome reprinting of this article provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7053."

[2] Assistant chemist, Explosives Division, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

[3] Scott, G. S., and Jones, G. W., Oxidation of Anthracite: Liberation of Carbon Monoxide and Its Relation to Ignition Temperature: Ind. Eng. Chem., vol. 29, 1937, pp. 106-108

[4] Scott, G. S., and Jones, G. W., Significance of Low-Temperature Oxidation Products in Mine-Fire Studies: Ind. Eng. Chem., vol. 29, 1937, pp. 822-826.

[5] Scott, G. S., and Jones, G. W., The Composition and Inflammability of Gaseous Distillation Products from Heated Anthracite: Bureau of Mines Rep. of Investigations 3378, 1938, 6 pp.

[6] Scott, G. S., and Jones, G. W., Oxidation of Anthracite: Effect of Time of Contact on the Concentration of Oxygen in the Effluent Gases: Bureau of Mines Rep. of Investigations 3405, 1938, 7 pp.

[7] Scott, G. S., and Jones, G. W., Effect of Oxidation on the Volatile Matter of Anthracite and Its Significance in Mine-Fire Investigations: Bureau of Mines Rep. of Investigations 3398, 1938, 8 pp.

[8] McElroy, G. E., Some Observations on the Causes, Behavior, and Control of Fires in Steep-Pitch Anthracite Mines: Bureau of Mines Inf. Circular 7025, 1938, 36 pp.

In the case of oxidation below the ignition temperature, the above conditions are altered considerably. First, laboratory tests have shown that the ratio of hydrogen to carbon in the gaseous oxidation products is highest at the start and decreases during the progress of oxidation. Since the heat of combustion of a unit weight of hydrogen is about four times as great as the heat of combustion of carbon, this would decrease the heat liberated per unit of oxygen consumed as the oxidation proceeds.

Second, the ratio of carbon monoxide to carbon dioxide increases with increasing temperature, and heat liberated decreases when the oxidation of carbon goes to carbon monoxide rather than carbon dioxide; this decrease is proportional to the relative amount of carbon monoxide formed.

Third, at temperatures up to the carbon monoxide inflection point, a part of the consumed oxygen is "fixed" by the coal, and thermal effects accompany this "fixation."

The problem resolves itself into finding the heat liberated at constant pressure when the following reaction takes place:

$$\text{Anthracite} + aO_2 = bCO_2 + cCO + dH_2O + e\text{Residue};\ \Delta H_1 = ? \tag{1}$$

Direct determinations of the heating value of the coal before and after low-temperature oxidation were made on numerous samples[9] by the Coal Analysis Section at the Central Experiment Station, Pittsburgh, Pa., which yielded ΔE_2 and ΔE_3 for

$$\text{Anthracite} + fO_2 = gCO_2 + hH_2O\ (1);\ \Delta E_2 = (\text{determined}), \tag{2}$$

$$e\text{Residue} + iO_2 = jCO_2 + kH_2O\ (1);\ \Delta E_3 = (\text{determined}). \tag{3}$$

Subtracting (3) from (2),

$$(\text{Anthracite} - e\text{Residue}) + (f - i)O_2 = (g-j)CO_2 + (h-k)\ (H_2O\ (1);\quad \Delta E_4 = \Delta E_2 - \Delta E_3. \tag{4}$$

The Δ E's represent heat exchanges at constant volume (in calorimeter bomb). To convert ΔE_4 to ΔH_4, heat exchanged at constant pressure, the processes

$$(h-k)\ H_2O\ (1) = (h-k)\ H_2O\ (g,\ 1\ \text{atm});\ \Delta H_5 = \Delta H_v, \tag{5}$$

$$nO_2\ (g,\ 1\ \text{atm}) = nO_2\ (\text{in residue});\ \Delta H_6 = +nRT. \tag{6}$$

(5) and (6) must be added to (4). This gives

$$(\text{Anthracite} - e\text{Residue}) + (f-i+n)\ O_2 = (g-j)\ CO_2 + (h-k)H_2O(g,\ 1\ \text{atm});\quad \Delta H_7 = \Delta E_4 + \Delta H_5 + \Delta H_6. \tag{7}$$

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[9] Work cited; see footnote 7.

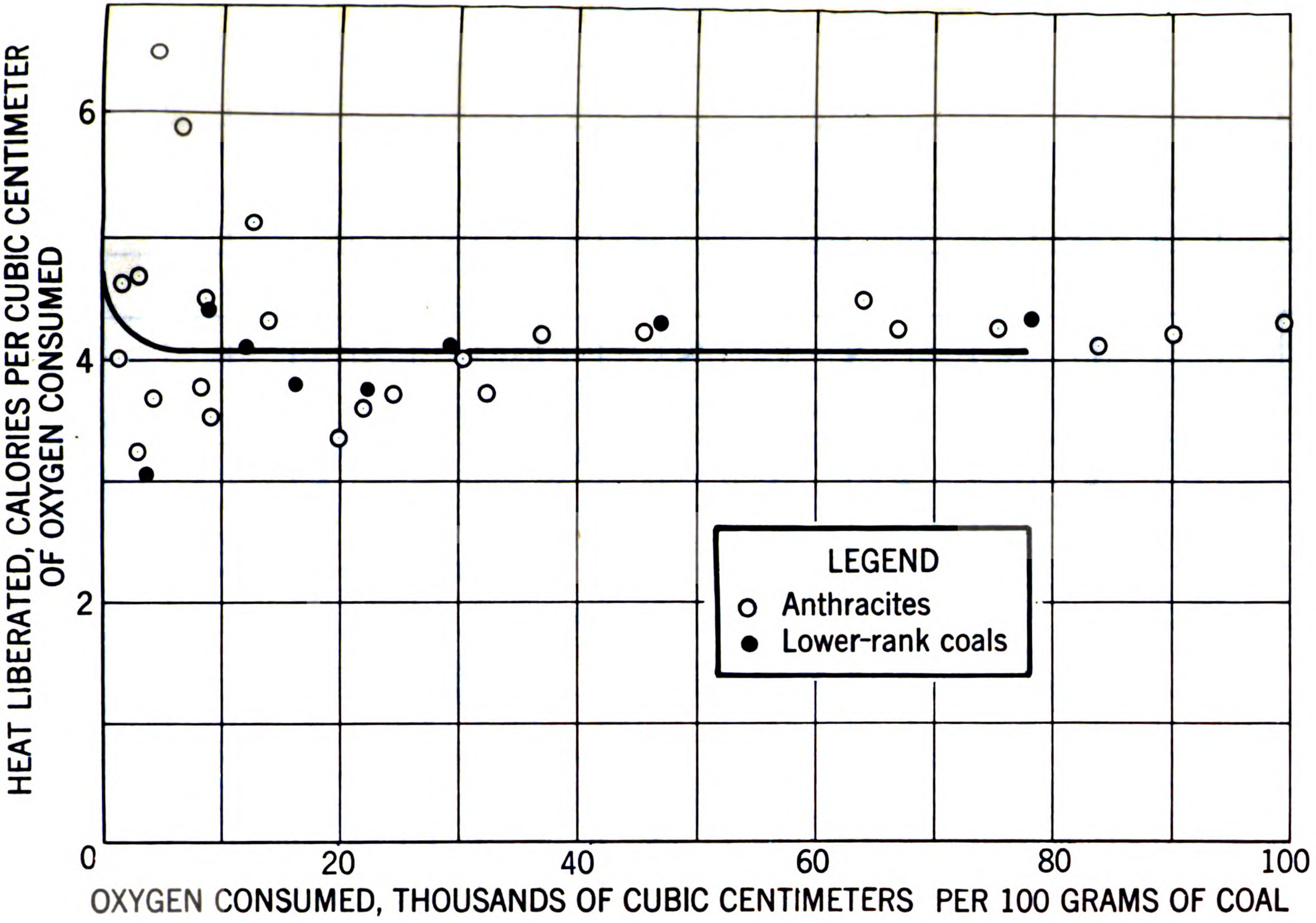

Figure 1.—— Average heat liberated during low-temperature oxidation of anthracites and some lower-rank coals.

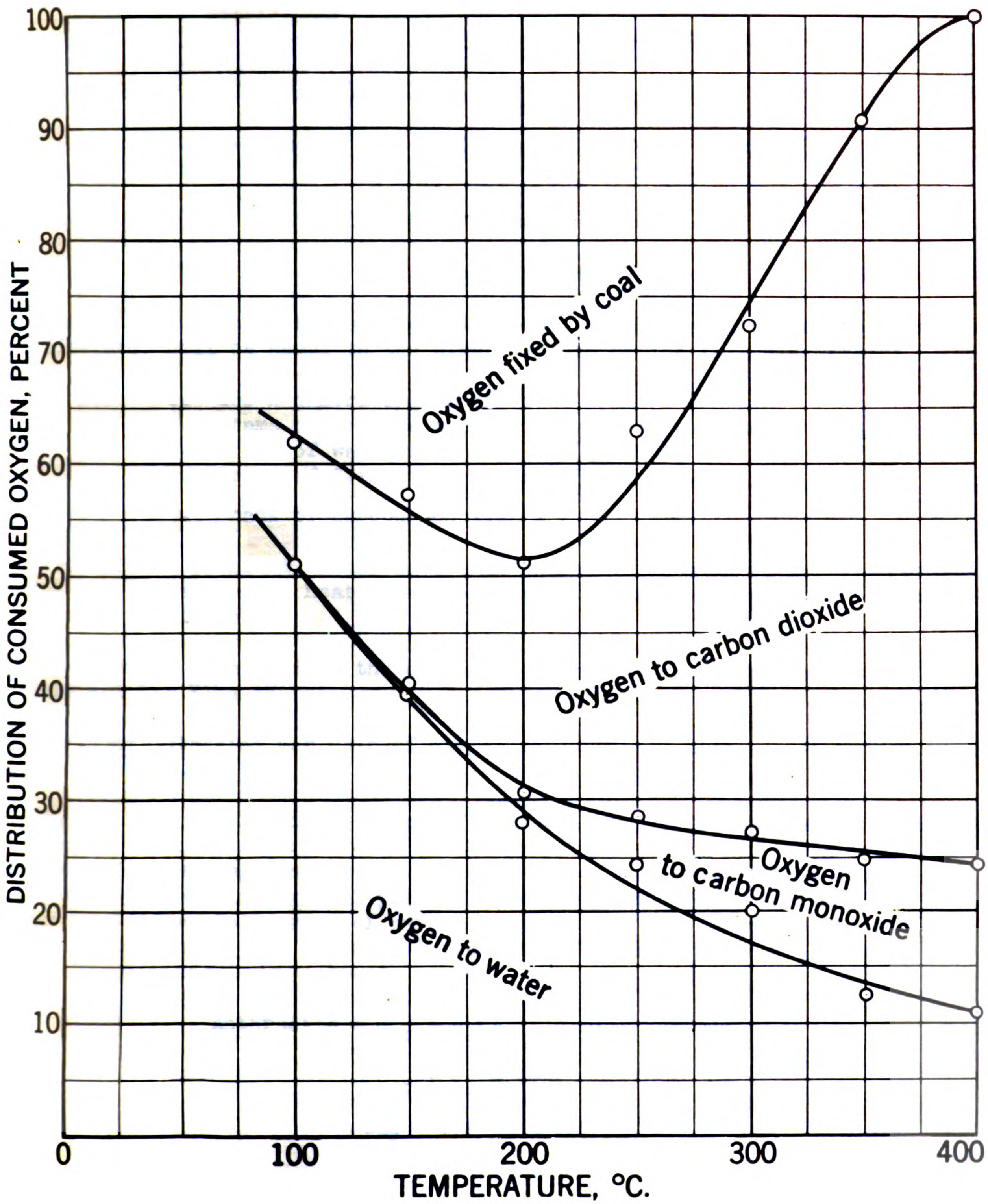

Figure 2.— Distribution of consumed oxygen. Oxidation of anthracite 16.

Equation (8)

$$cCO + pO_2 = mCO_2; \Delta H_8 = \text{(known)} \qquad (8)$$

may now be subtracted from (7) to give

$$\text{(Anthracite-eResidue)} + (f-i+n-p)O_2 = (g-j-m)CO_2 + (h-k)H_2O(g) + cCO; \quad \Delta H_9 = \Delta H_7 - \Delta H_8. \qquad (9)$$

Equation (9) is identical with (1), and

$$\Delta H_9 = \Delta H_1 = \Delta E_2 - \Delta E_3 + \Delta H_v + nRT - \Delta H_8.$$

Thus, if 100 grams of fresh coal is taken for the basis of calculation, the heat liberated will be equal to the algebraic sum of the following items:

1. 100 x calories/gram of fresh coal $(= \Delta E_2)$.
2. Grams of residue x calories/gram of residue $(= \Delta E_3)$.
3. Grams of water x (-583) $(= \Delta H_v)$.
4. Grams of "fixed" oxygen x $\frac{2 \times 597}{32}$ $(= nRT)$.
5. Grams of carbon monoxide x 2,415 $(= \Delta H_8)$.

Table 1 was compiled by making use of the above equations, and the results showing the variations of heat liberated per cc of oxygen consumed are shown graphically in figure 1.

The thermal data used in the calculations were taken from the compilation of Lewis and Von Elbe.[10]

The heat liberated per unit of oxygen consumed may also be determined by an alternate method.

Figure 2 shows the distribution of consumed oxygen for anthracite 16 during 72 hours at various temperatures. If the proportion of oxygen going into the formation of each component at any selected temperature be multiplied by the heat quantity accompanying that process, the sum of the products gives the average heat liberated per cc of oxygen consumed for the 72-hour period at that selected temperature. In the calculation, the following processes were considered:

$$\text{Anthracite} = C_{gr} + H_2(g, 1\ \text{atm}) + \text{residue}, \qquad (10)$$

$$C_{gr} + O_2 = CO_2, \qquad (11)$$

$$C_{gr} + 1/2\ O_2 = CO, \qquad (12)$$

$$H_2(g) + 1/2\ O_2 = H_2O\ (g), \qquad (13)$$

$$\text{Residue} + O_2 = O_2 \text{ (in residue)}. \qquad (14)$$

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[10] Lewis, B., and von Elbe, G., Combustion, Flames, and Explosions: Macmillan Co., New York, 1938, p. 384.

TABLE 1. - Heat liberated in low-temperature oxidation of anthracites and some other coals

Sample	Temperature of oxidation, °C	Coal	Residue			Water		Carbon monoxide		Calories liberated	Oxygen consumed	Calories/cc O_2
		100 x calories/grams	Weight grams	Calories/grams	Calories	Weight, grams	Calories	Weight, grams	Calories			
Anthracites												
16	150	786,100	100.57	7,750	779,417	1.031	600	0.034	82	6,001	1,497	4.01
	200		100.99	7,628	770,352	2.248	1,309	-	-	14,439	3,100	4.66
	200		101.43	7,639	774,824	1.391	810	.249	601	9,865	3,051	3.23
	250		102.14	7,056	713,644	4.501	2,620	1.671	4,035	65,801	12,850	5.12
	300		101.34	6,711	680,093	7.916	4,609	4.339	10,479	90,919	24,600	3.70
	350		70.75	5,900	417,425	15.118	8,802	21.435	51,766	308,107	72,500	4.25
	400		41.05	6,340	260,257	16.824	9,795	34.992	84,506	431,542	99,500	4.34
9	250	529,400	100.31	4,972	498,741	2.316	1,348	.383	925	28,386	4,370	6.50
	350		85.70	3,544	303,721	9.880	5,752	11.378	27,478	192,449	45,800	4.20
19	250	617,800	101.49	5,733	581,842	3.552	2,068	1.046	2,526	31,364	8,380	3.74
S-1	350	652,800	94.05	5,433	510,974	6.310	3,674	7.267	17,550	120,602	32,300	3.73
32	250	636,700	101.02	5,872	593,189	2.783	1,620	.761	1,838	40,053	6,820	5.87
	350		76.62	3,967	303,952	11.219	6,532	18.878	45,590	280,626	63,900	4.48
33	250	690,600	101.09	6,389	645,864	3.221	1,875	1.327	3,205	39,656	8,840	4.49
	350		72.28	4,894	353,738	11.08	6,451	18.85	45,523	284,888	67,150	4.24
34	300	539,400	98.50	4,561	449,258	6.79	3,953	3.085	7,450	78,739	21,800	3.61
36	200	703,000	100.42	6,910	693,915	.793	462	.248	599	8,024	1,748	4.59
	250		100.78	6,790	684,296	1.951	1,136	.711	1,717	15,851	4,315	3.67
	300		100.70	6,610	665,627	2.602	1,515	1.640	3,961	31,897	9,035	3.53
	350		93.96	5,960	560,001	5.767	3,358	7.690	18,571	121,070	30,220	4.01
	400		57.71	5,139	296,572	11.328	6,595	23.765	57,392	342,441	83,800	4.08
40	300	590,000	98.63	5,178	510,706	4.822	2,807	3.912	9,447	67,040	20,020	3.35
16B	300	797,000	68.05	4,975	338,548	16.05	9,350	28.92	69,842	379,260	90,200	4.20
	350	797,200	90.55	6,772	613,205	8.258	4,808	9.848	23,783	155,404	36,910	4.21
	300	797,000	21.77	3,050	66,398	22.24	13,065	44.78	108,144	609,393	141,600	4.30

TABLE 1. - Heat liberated in low-temperature oxidation of anthracites and some other coals (Continued)

Sample	Temperature of oxidation, °C	Coal	Residue			Water		Carbon monoxide		Calories liberated	Oxygen consumed	Calories/cc O_2
		100 x calories/grams	Weight grams	Calories/grams	Calories	Weight, grams	Calories	Weight, grams	Calories			
Bituminous												
41	150	760,000	103.87	6,949	720,857	4.75	2,765	.420	1,014	34,964	7,900	4.43
	250		97.59	5,350	522,106	25.84	15,044	7.71	18,620	204,230	47,330	4.31
31	200	812,800	105.89	6,755	715,287	13.776	8,020	2.522	6,091	83,402	22,190	3.76
	300		72.65	5,700	414,105	31.871	18,555	16.965	40,970	339,170	78,300	4.33
Subbituminous												
22	150	665,500	102.96	5,922	609,729	7.322	4,263	.984	2,376	49,132	11,990	4.10
	200		98.38	5,328	524,169	17.373	10,115	4.245	10,252	120,964	29,300	4.13
26	100	678,300	100.93	6,583	664,422	2.670	1,555	.217	524	11,799	3,850	3.06
	150		100.47	6,033	606,136	9.464	5,510	2.010	4,854	61,800	16,310	3.79

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That is to say, the coal may arbitrarily be assumed to decompose first into graphitic carbon, gaseous hydrogen, and a solid residue. The graphitic carbon then unites with oxygen to form carbon dioxide and carbon monoxide. The hydrogen unites with oxygen to form water. Oxygen enters the residue to form a complex. The thermal changes accompanying (11), (12), and (13) are 4.199, 2.358, and 5.163 calories per cc of oxygen, respectively.

To obtain thermal values for equations (10) and (14), table 2 was constructed. In this table, columns 1, 2, and 3 are self-explanatory and for reference only. Columns 4, 5, 6, and 13 are the moisture- and ash-free percentages of hydrogen, carbon, sulphur, and oxygen in the coal or residue. These percentages of hydrogen, carbon, and sulphur (divided by 100) are multiplied by 34,327, 7,836, and 2,500, respectively, the products appearing in columns 7, 8, and 9 and the sums in column 10. The figures in column 10 represent the heat evolved when graphitic carbon, gaseous hydrogen, and solid sulphur are burned in a bomb in the proportions of the analyses. If these figures are subtracted from the observed calorific values (shown in column 11), the heat of formation of each particular sample of coal from graphitic carbon, gaseous hydrogen, and sulphur at constant volume is obtained (column 12).

In figure 3 these heats of formation have been plotted against oxygen contents. The mineral matter in the coal and in the ash may be in different forms especially at a temperature of 350°C. Thermal effects accompany these changes and may explain part of the differences between samples.

The slopes of the lines in figure 3 appear to be constant. Since the slop represents the thermal change accompanying "fixation" of oxygen by anthracite, it is desirable to obtain the best value afforded by the data.

This was done by the method of least squares.[11] Equations of these lines are of the form

$$y = a + bx,$$

where y = heat of formation of the coal and x = percentage of oxygen. To make the sum of the squares of the deviations a minimum,

$$(\Sigma\triangle^2 = \Sigma (a + bx - y)^2 = (\text{minimum}),$$

the first differential with respect to each constant must equal zero; that is,

$$\frac{d\Sigma\Delta^2}{da} = 2\Sigma(a = bx - y) = a\Sigma + b\Sigma x - \Sigma y = 0,$$

$$\frac{d\Sigma\Delta^2}{db} = 2\Sigma(a + bx - y)x = a\Sigma x + \Sigma b\Sigma x^2 - \Sigma xy = 0.$$

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[11] See, for example, Steinmetz, C. P., Engineering Mathematics: McGraw-Hill Book Co., New York, 1917, pp. 179-186.

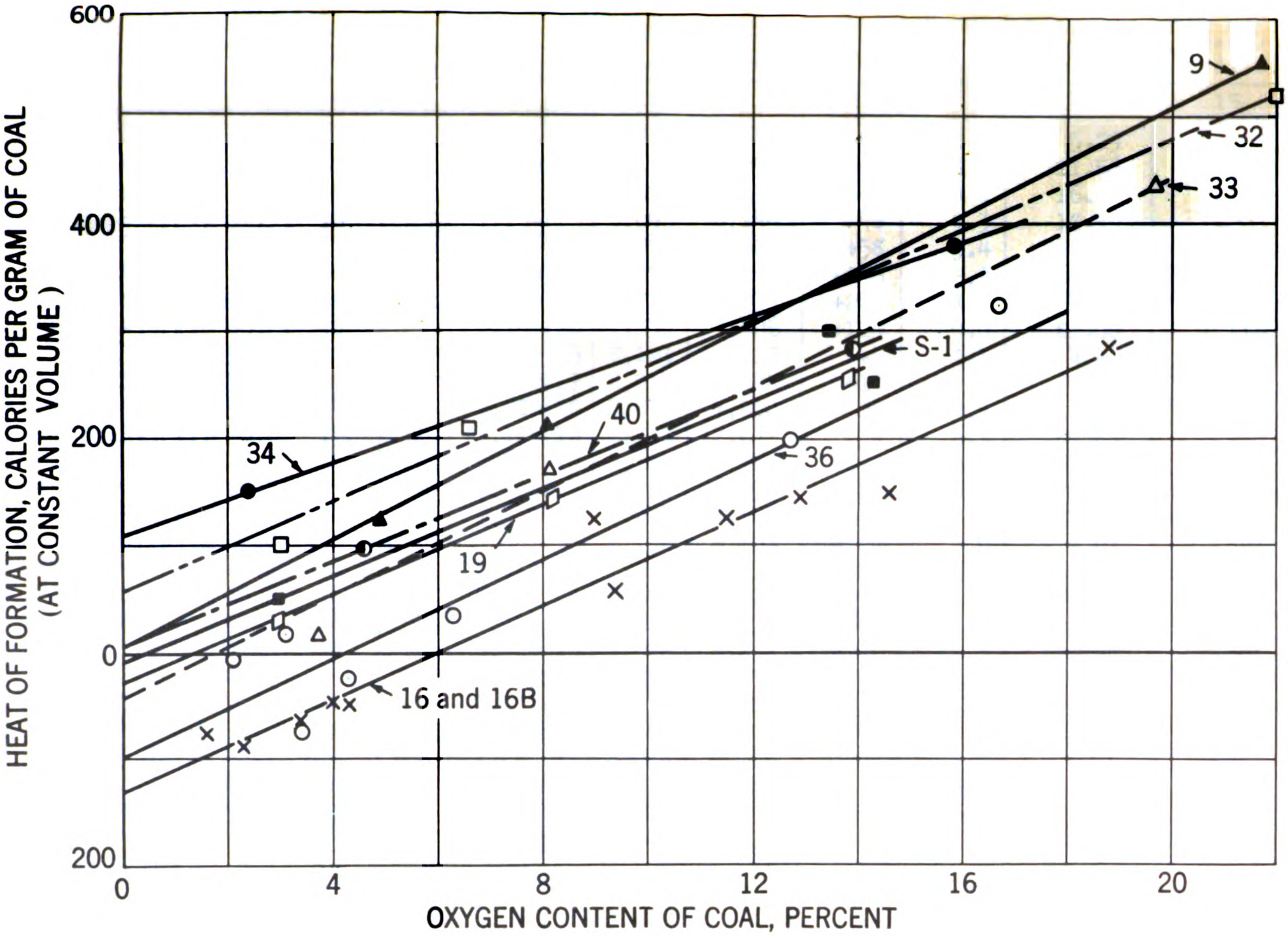

Figure 3. —— Heats of formation of different anthracites from graphite and hydrogen.

No.	°C.	Dry ash	Moisture and ash free, percent			Calories from –			Total calories		Diff.	O_2 per-cent	(O_2 per-cent)^2	(O_2 per-cent) x diff.
			H	C	S	H	C	S	Calc.	Obs.				
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
16	25	6.0	2.8	93.1	0.7	961	7,295	17	8,273	8,361	-88	2.3	5.29	-202
	150	6.1	2.8	92.0	.7	961	7,209	17	8,187	8,250	-63	3.4	11.56	-214
	200	6.2	2.6	91.7	.6	893	7,186	15	8,094	8,139	-45	4.0	16.00	-180
	200	6.2	2.7	91.3	.6	927	7,154	15	8,096	8,144	-48	4.3	18.49	-206
	250	6.0	2.2	86.6	.7	755	6,786	17	7,558	7,500	+58	9.4	88.36	545
	300	6.1	2.2	83.2	.6	755	6,520	15	7,290	7,144	+146	12.9	166.41	1,883
	350	8.3	1.9	77.2	.6	652	6,049	15	6,716	6,433	+283	18.8	353.44	5,320
	400	14.4	2.2	86.2	.8	755	6,755	20	7,530	7,406	+124	9.0	81.00	1,116
36	25	13.5	2.0	94.7	.6	687	7,421	15	8,123	8,128	-5	2.1	4.41	-10
	200	13.8	1.9	93.7	.7	652	7,342	17	8,011	7,994	+17	3.1	9.61	53
	250	14.1	1.7	92.9	.4	584	7,280	10	7,874	7,900	-26	4.3	18.49	-112
	300	13.9	1.7	90.8	.5	584	7,115	12	7,711	7,677	+34	6.3	39.69	214
	350	14.4	1.5	84.7	.5	515	6,637	12	7,164	6,967	+197	12.7	161.29	2,502
	400	20.2	1.3	80.5	.3	446	6,308	7	6,761	6,439	+322	16.7	278.89	5,377
	450	16.9	1.7	93.8	.4	584	7,350	10	7,944	8,017	-73	3.4	11.56	-248
9	25	34.1	3.1	89.8	.6	1,064	7,037	15	8,152	8,028	+124	4.9	24.01	608
	250	34.4	2.8	87.0	.5	961	6,817	12	7,790	7,578	+212	8.1	65.61	1,717
	350	40.0	1.9	73.8	.6	652	5,783	15	6,450	5,900	+550	21.7	470.89	11,935
S-1	25	18.4	2.3	93.5	.4	790	7,327	10	8,127	8,078	+49	2.9	8.41	142
	350	20.5	1.7	82.8	.4	584	6,488	10	7,082	6,833	+249	14.3	204.49	3,561
	350	20.5	1.7	83.5	.4	584	6,543	10	7,137	6,839	+298	13.4	179.56	3,993
40	25	25.8	2.6	91.0	.8	893	7,131	20	8,044	7,950	+94	4.6	21.16	432
	300	24.9	2.1	82.2	.8	721	6,441	20	7,182	6,900	+282	13.9	193.21	3,920
34	25	33.3	2.8	92.4	1.5	961	7,240	37	8,238	8,085	+153	2.4	5.76	367
	300	31.9	2.2	80.5	.6	755	6,308	15	7,078	6,700	+378	15.9	252.81	6,010
33	25	14.4	2.5	91.9	.9	858	7,201	22	8,081	8,067	+14	3.7	13.69	52
	250	14.9	2.3	87.7	.9	790	6,872	22	7,684	7,511	+173	8.1	65.61	1,401
	350	20.6	1.7	76.5	.7	584	5,994	17	6,595	6,161	+434	19.7	388.09	8,550

TABLE 2. (Continued)

No.	°C	Dry ash	Moisture and ash free percent			Calories from -			Total calories		Diff.	O_2 per-cent	(O_2 per-cent)^2	(O_2 per-cent) x diff.
			H	C	S	H	C	S	Calc.	Obs.				
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
32	25	21.4	2.8	92.1	1.1	961	7,217	27	8,205	8,106	+99	3.0	9.00	297
	250	22.8	2.4	88.9	1.2	824	6,956	30	7,820	7,611	+209	6.6	43.56	1,379
	350	31.9	1.5	74.0	1.0	515	5,799	25	6,339	5,822	+517	22.0	484.00	11,374
19	25	25.0	3.1	91.5	1.3	1,064	7,170	32	8,266	8,239	+27	2.9	8.41	78
	250	24.6	2.7	86.6	1.3	927	6,786	32	7,745	7,600	+145	8.2	67.24	1,189
	300	25.0	2.3	81.5	1.4	790	6,386	35	7,211	6,956	+255	13.8	190.44	3,519
16B	25	5.3	2.9	93.5	.8	995	7,327	20	8,342	8,417	-75	1.6	2.56	-120
	300	8.0	1.3	70.0	.7	446	5,435	17	5,948	5,411	+537	26.3	691.69	14,123
	250	6.1	2.1	84.1	1.1	721	6,590	27	7,338	7,211	+127	11.5	132.25	1,460
	375	9.0	1.9	80.9	.7	652	6,339	17	7,008	6,861	+147	14.6	213.16	2,146
Total			83.9	3,288.1	28.4						5,719	356.8	5,000.10	93,971

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In table 2, values for x^2 and xy are shown in columns 14 and 15, and the following equations were obtained by proper substitution of the sums,

$$38a + 356.8b - 5{,}719 = 0,$$
$$356.8a + 5{,}000.1b - 93{,}971 = 0.$$

Solving simultaneously gives

$$a = -78.7,$$

$$b = 24.409,$$

and

$$\text{heat of formation} = -78.7 + 24.409\ (O_2\ \text{percent})\ \text{cals./gram.}$$

The heat evolved when oxygen is "fixed" by anthracite is, then,

$$24.409 \times 100 \times \frac{1{,}429}{1{,}000} = 3.488\ \text{calories/cc oxygen}$$

at constant volume, and 3.515 calories per cc of oxygen at constant pressure.

These data are used in table 3. To each sum must be added the heat of decomposition of the coal. For no. 16 this is +88 calories per gram at constant volume, which becomes 80 calories per gram at constant pressure. Assuming 1900 cc oxygen consumed per gram of coal, this becomes 0.042 calories per cc of oxygen. The results are plotted on figure 1 as a smooth curve.

TABLE 3. - Alternate calculation of the heat liberated by low-temperature oxidation

Temp., °C.	Consumed oxygen Distribution	Fraction	H calories/cc	Product	Sum + 0.042 = calories/cc O_2 consumed	Oxygen consumed, cc/100 grams coal
100	Fixed	0.375	3.515	1.318		
	To CO_2	.115	4.199	.483		
	To H_2O	.510	5.163	2.633	4.476	242
200	Fixed	.485	3.515	1.705		
	To CO_2	.205	4.199	.861		
	To CO	.025	2.358	.059		
	To H_2O	.285	5.163	1.471	4.138	2,712
250	Fixed	.415	3.515	1.459		
	To CO_2	.310	4.199	1.302		
	To CO	.060	2.358	.141		
	To H_2O	.215	5.163	1.110	4.054	6,960
300	Fixed	.260	3.515	.914		
	To CO_2	.480	4.199	2.016		
	To CO	.090	2.358	.212		
	To H_2O	.170	5.163	.878	4.062	24,620
350	Fixed	.090	3.515	.316		
	To CO_2	.655	4.199	2.750		
	To CO	.120	2.358	.283		
	To H_2O	.135	5.163	.697	4.088	77,270

Discussion of Results

It will be observed that the calculated heat liberated per cc of oxygen consumed by anthracite at oxidation temperatures ranging from 150° to 400° C. ranged from 3.23 to 6.50 calories. However, all of the values obtained when the oxidation tests were made at 350° and 400° C. lie close to an average range of 4.00 to 4.25 calories.

The calculated heat liberated per cc of oxygen consumed when bituminous and subbituminous coals were tested ranged from 3.06 to 4.43 calories, as shown in table 1.

The only direct determination of the heat liberated by low-temperature oxidation of which the author is aware was made by Lamplough and Hill,[12] who found a mean value of 3.3 calories per cc of oxygen consumed for -30-mesh coal at normal temperatures.

They state that when carbon is burned to CO_2 and to CO, 4.4 and 2.6 calories per cc O_2 are liberated, respectively, but do not mention the formatio of water, which in anthracite takes a considerable proportion of the consumed oxygen in the early stages and liberates 5.16 calories per cc O_2.

It is possible that the lower figure obtained by Lamplough and Hill may be due to the presence of larger quantities of pyrite than are found in Pennsylvania anthracite.

12/ Lamplough, F. E. E., and Hill, A. M., The Slow Combustion of Coal Dust an Its Thermal Value: Trans. Inst. Min. Eng., vol. 45, 1912-13, pp. 629-65